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CARBON & GRAPHITE SURFACE PROPERTIES RELEVANT TO FIBER REINFORCED COMPOSITES

R. DIDCHENKO

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION

TECHNICAL REPORT AFML-TR-68-45
FEBRUARY 1968

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CARBON AND GRAPHITE SURFACE PROPERTIES
RELEVANT TO FIBER REINFORCED COMPOSITES

R. Didchenko

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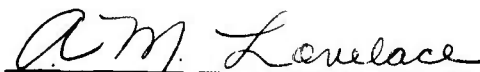
FOREWORD

The work reported herein was performed under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Air Force Materials Laboratory, MAN, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, Contract No. AF 33(615)-3110, ARPA Order No. 719, Program Code 5D10. Mr. H. S. Schwartz, MAN is the Air Force Program Manager. The manuscript was released by the author February 1, 1968, for publication.

The Contractor is Union Carbide Corporation, Carbon Products Division, Parma Technical Center, P. O. Box 6116, Cleveland, Ohio 44101. The author of this Technical Report is Dr. R. Didchenko. Dr. G. B. Spence is the Program Supervisor.

The author wishes to recognize the major contribution to this report by Dr. P. D. Coulter, who was responsible for the measurements of the surface properties and for the interpretation of the data. The staff of the Technical Information Service at the Parma Technical Center was very helpful in collecting the material for the bibliography.

This technical report has been reviewed and is approved.



A. M. Lovelace

Director

Air Force Materials Laboratory

ABSTRACT

The bibliography presented in the first part of this report lists literature sources on the surface properties of carbon and graphite, in bulk and fiber form, selected from the point of view of their relevance to the technology of composite materials. The topics considered are: morphology, surface compounds, wetting and adsorption properties of different forms of carbon, and the results of studies specifically directed toward modifying the surface of carbon and graphite fibers in order to improve their performance in composites.

The second part contains the most recent experimental data on mercury density, pore-size distribution and surface area of low modulus carbon and graphite fibers, and of high modulus "Thornel" 25* and "Thornel" 40 fibers. Some preliminary results of surface treatment of "Thornel" 40 with chromic acid solution are also given.

*"Thornel" is a trademark of Union Carbide Corporation for High Modulus Graphite Yarn

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SECTION I

INTRODUCTION

The potential of high modulus carbon fibers for the reinforcement of composite materials is well recognized by the workers in the field. Studies of various fiber-matrix systems which appear attractive for different applications indicate that, in many cases, the full potential of the high modulus carbon fibers may be exploited only through a significant improvement of interlaminar shear strength. This result probably can be achieved by improving the adhesion between the carbon filaments and the matrix. The adhesion is profoundly affected by the surface properties of the fiber. These properties may determine the choice of the matrix, or, if the matrix is fixed by other considerations, some modifications of the surface may be required in order to achieve the best possible adhesion. These modifications usually involve changes in the surface morphology (surface area, roughness, pore-size distribution, etc.) or changes in the chemical functionality of the surface such as the formation of oxides, active sites, etc. Finally, if none of these treatments improve the adhesion, the use of coupling agents may be necessary to overcome some basic incompatibility of the system, as was the case in the fiber glass technology.

We hope that the information contained in this report will be useful to the workers concerned with interfacial phenomena in the carbon fiber composites. In Section II, we present a selective bibliography with short abstracts which should be sufficient to help the reader in the choice of papers to study as the background for his particular field of interest. In view of the relative dearth of information on the physical and chemical properties of surfaces of carbon fibers, most of the bibliography refers to the surface properties of bulk carbon and graphite. The reader is cautioned that, although much of this information is undoubtedly relevant, it is very likely not directly applicable to the different forms of carbon fibers.

Section III of this report contains some recent data on physical surface properties of carbon and graphite yarns. The information on the pore-size distribution is being published for the first time. The surface area data on "Thornel" 25 and "Thornel" 40 should help to resolve some of the discrepancies found in the literature (see Section II E, references 6 and 16). Results obtained on "Thornel" 40 yarn etched with chromic acid solution have been included because they seem to be the first piece of evidence that the pore-size distribution may be an important factor influencing the interlaminar shear strength.

SECTION II

BIBLIOGRAPHY OF SURFACE PROPERTIES OF BULK AND FIBER MATERIALS

The papers included in this bibliography were selected because, in the opinion of the author, they have some, if sometimes only limited, relation to the previously outlined avenues of approach to the problems of adhesion. The reader unfamiliar with the great heterogeneity of carbon materials, particularly with regard to their surface properties, should be aware that the surface behavior of, for example, Graphon ("Spheron 6" carbon black, heated to 2000°C, produced by Cabot Co., Ltd.) may be used only as a guide line as to what may occur on the surface of "Thornel" fibers under identical conditions. With many other types of carbons, there may be no correlation at all.

The topics considered in this bibliography are as follows:

- A. Morphology of Carbon Surfaces
- B. Surface Oxides and Other Surface Compounds of Carbon
- C. Wetting Properties of Carbon
 - 1) Thermodynamics
 - 2) Contact Angles
- D. Adsorption Properties of Carbon
- E. Literature Specifically Related to Surface Properties of Carbon and Graphite Fibers

It was not always possible to adhere consistently to this classification, since adsorption and oxidation studies are often related to morphology and even the contact angles are affected by the so-called "roughness factor". For this reason, bits of morphological information are scattered through the entire literature on carbon, although no single satisfactory organized source of information is available.

The study of the surface oxides of carbon, i. e. the chemical modification of the carbon surface by oxidation, has been a very active field of research for many years, and several excellent, up-to-date reviews by experts are extant concerning which nothing could be added by the present bibliography. Therefore, in Section II B, we shall simply give a short description of these review articles. In addition, we list a number of papers which were either not considered by the reviewers or were published at a later date.

The wetting properties of carbon have not received yet the critical attention of an expert reviewer, nor does the present writer consider himself qualified to do justice to the subject. For this reason, Section II C will be presented as compilation of papers, alphabetically arranged according to the authors, followed by a short synopsis of their contents which should be sufficient to simplify for the reader the task of

selecting appropriate papers. It should be realized, however, that measurements of contact angles and heats of immersion on poorly defined materials are notorious for their irreproducibility and should be always considered in the full context of experimental details and qualifying comments of the authors. This information cannot be reflected in the abstract. The studies of wetting by metals, molten salts, and refractory compounds were included not only because of their scientific interest, but also because some of these materials are being considered as coupling agents or surface treatments for carbon in resin bonded composites.

In Section II D, the writer of this bibliography had to be particularly selective in order not to open the flood gate to the vast sea of literature on activated carbon which would be of very marginal relevance to the intended readers. The few papers which are offered for consideration tend to emphasize the electrochemical and ion-exchange aspects of carbon surface interacting with solutions, again because of their possible implications in the field of adhesion.

Section II E lists papers and government contract reports directly related to carbon fibers with regard to surface properties, surface treatments, coatings, etc. directed at improvements of the bonding at the fiber-matrix interface.

A. Morphology of Carbon Surfaces

The most comprehensive and entirely unique compilation of the present knowledge of the surface morphology of different types of carbon may be found in the second volume of Les Carbones published under the direction of A. Pacault by the "Groupe Francais D'Etudes des Carbones" Masson et C^{ie}, Paris, 1965 (2 Volumes, in French). Chapter XV of this volume (pp. 161-232) authored by M. Bastick, P. Chiche, and J. Rappeneau contains a wealth of information on surface areas, pore-size spectra, and gas permeabilities of practically all known grades of carbon, even those prepared only on laboratory scale from various polymers, including cellulose. Even the reader unfamiliar with the French language will gain a great deal of information from the perusal of the thirteen tables of data and of the seventeen figures, the captions of which can be easily understood with the help of a dictionary. The chapter contains 149 literature references.

A much less useful, from our point of view, but nevertheless, relevant review is the second chapter of Chemistry and Physics of Carbon, Vol. 2, Philip L. Walker, Ed., Marcel Dekker, New York, 1966, (pp. 51-120) written by M. M. Dubinin and entitled "Porous Structure and Adsorption Properties of Active Carbons." As the title indicates, this article is concerned exclusively with the activated carbons. Nonetheless, it contains a great deal of fundamental information pertinent to all carbon bodies, their surface properties, and their interactions with vapors and gases. Among sixty references, fifty-one are to Russian sources, somewhat limiting their usefulness.

The same general subject is discussed in greater depth, but in much more diffuse form, in the recent book Adsorption Surface Area and Porosity by S. J. Gregg and K. S. W. Sing, Academic Press, 1967, which contains numerous references to carbon surface properties.

A great deal of morphological information obtained by optical methods may be found in the "Microscopic Studies of Graphite Oxidation," by J. M. Thomas in the Chemistry and Physics of Carbon, Vol. I, Chapter IV, pp. 121-202. Thirty-seven figures (mostly optical but also including some electron micrographs) show the effects of treatment of simple crystals of graphite by molecular and atomic oxygen, nitric oxide, and carbon dioxide on the formation of etch pits on the basal plane of graphite. A large portion of the work concerns the role of metallic catalysts in promoting the oxidation of graphite. The chapter contains 141 references.

The most recent work on this subject is reported in: C. Roscoe and J. M. Thomas, "The Revelation of Small-Angle Boundaries and Forest Dislocations in Graphite Monocrystals" Carbon 4, 383-490, 1966.

B Surface Oxides of Carbon

The first review on this subject by R. N. Smith, "Chemistry of Carbon-Oxygen Surface Compounds" Quart. Revs. (London) 13, 287-305 (No. 9, 1959) contains 30 references (dating back to the year 1815) and stresses the preparative aspects, oxidation in liquid phases, and the practical implications of the carbon surface compounds in the field of catalysis, adsorption, friction, etc.

Perhaps the best, quickest, up-to-date introduction to the subject of surface properties of carbon may be found in the first three sections of a paper by H. P. Boehm on the "Functional Groups on the Surface of Solids." Angewandte Chemie, Internat. Ed. 5, 533-622 (1966). The section on the "Surface Compounds on Diamond-Like Structures" is particularly valuable, since this subject has not been reviewed elsewhere. The review contains 45 references, mostly in the field of the so-called "surface complexes" which result from the oxidation of carbon surfaces. The review covers the literature through 1964 rather thoroughly with the emphasis on interaction of the carbon surfaces with the gas phase and on the structural aspects of the surface compounds.

This paper is a condensed version of a chapter by the same author entitled "Chemical Identification of Surface Groups" in Advances in Catalysis, Vol. 16, Academic Press, 1966, pp. 179-267, which covers the subject of carbon in the first forty-four pages. In addition to a very thorough treatment of surface oxides, this chapter also contains references to surface sulfides and chlorides, to the chemisorption of hydrogen and to the chemical fixation of free radicals on the surface. The study of this chapter is highly recommended to anyone contemplating

work involving carbon surfaces because of the authoritative critical treatment of the subject and the valuable compilation of 158 references which cover very thoroughly the publication of American and West European workers through 1964. Some idea of the trends of research on carbon surfaces taking place in the Soviet Union may be obtained from the article (in English) by A. V. Kiselev on the "Nature of Adsorption on Graphitized and Oxidized Carbon Blacks" in Physico Chimie du Noir de Carbone, (Colloques Nationaux de Centre Nationale de la Recherche Scientifique, Paris 1963), which, according to the author, "attempts to consider, from a unified point of view, the nature of nonspecific and specific interactions during adsorption of molecules having different geometrical structure for a number of cases, in order of growing complexity." For the reader of this bibliography, who presumably is primarily interested in wetting properties of differently treated carbon, the most valuable portion of this paper describes the effect of various oxidative treatments of carbon surfaces on the absorption of organic molecules which have different degrees of polarity, with or without a π electron system, etc. Additional value for those familiar with the Russian language may be derived from the fact that of 98 references, 49 are from Russian sources, mostly items not mentioned in other reviews. It may be noted parenthetically that the entire volume of Physico Chimie du Noir de Carbone contains many original contributions by internationally recognized authorities in the surface chemistry of carbon, some of which are not referred to in the reviews previously cited here. This volume of the proceedings constitutes by itself a good literature source, particularly since carbon black has structural surface characteristics probably most closely related to those of graphite fibers. If the entire volume is not available, the following references are suggested as particularly relevant from our point of view:

1. J. B. Donnet and J. C. Benland, "Study of internal structure of some carbon blacks," Physico Chimie du Noir de Carbone, (Colloques Nationaux de Centre Nationale de la Recherche Scientifique, Paris 1963), *ibid.*, 51-9 (in French).

Includes effects of oxidation by air and nitric acid.

2. J. B. Donnet and J. Metzger, "Kinetics of fixation of free radicals on the surface of carbon black," *ibid.*, pp. 67-71 (in French).

Kinetics of isobuturonitrile fixation indicate that several mechanisms occur, since the curve showing the number of fixed radicals as a function of temperature passes through a maximum.

3. J. B. Donnet and A. Reiss, "The radical character of carbon blacks," *ibid.*, pp. 61-65.

The concentration of free valencies and of quinoid groups on the surface is determined by means of isobuturonitrile and of reducing agents, respectively. The results indicate that the unpaired electron is located either on the aromatic ring or on a peroxide group.

4. H. P. Boehm, E. Diehl and W. Heck, "Surface oxides on carbon black and other carbons," *ibid.*, pp. 91-6 (in German).

Carbon black and sugar charcoal were oxidized by means of oxygen or by oxidizing solutions (NaOCl , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ etc.) By titration with bases of varying strength, it was shown that the acid groups on the surface have different strengths. Further characterization by methylation, saponification, reactions with SOCl_2 , NH_3 and dinitrofluorobenzene indicated that the acid groups are present in forms of carboxyls, lactones, and phenolic hydroxyls.

(N. B. This paper is identical to reference 46 in the "Chemical Identification of Surface Oxides" by H. P. Boehm).

5. W. J. de Bruin and Th. Van der Plas, "Analyses of functional groups on the surface of carbon blacks," *ibid.*, pp. 83-90 (in English).

Analytical methods based on exchange processes and on formation of derivatives are described. The results indicate the existence of both lactone groups and, possibly, hydrogen bonded carbonyl-hydroxyl group combinations.

6. F. M. Lang and J. B. Donnet, "Air oxidation of carbon blacks at 620°C ," *ibid.*, pp. 103-6 (in French).

The presence of moisture decreases the rate of oxidation in agreement with observations made on all porous graphites. Internal micropores are not produced during oxidation.

Several more papers not included in the reviews must be mentioned in this context:

7. J. B. Donnet and E. Papirer, "Oxidation of carbon blacks by ozone," *Bull. Soc. Chem. France*, 1965, 1912-15 (in French).

Ozone produces a highly hydrophilic surface on carbon black. The X-ray and electron diffraction studies show a preferential attack on the least crystalline portions of the particles.

8. P. J. Hart, F. J. Vastola and P. L. Walker, Jr., "Oxygen chemisorption on well-cleaned carbon surfaces," *Carbon* 5, 363-71 (1967).

Graphon, a highly graphitized carbon black, was first oxidized to 14.4% weight loss in O_2 at 625°C to introduce significant active surface area. Following the cleaning of the activated Graphon surface by heating at 975°C in a vacuum of 10^{-8} torr, chemisorption of oxygen between 25 - 400°C was studied. The saturation amounts of oxygen adsorbed sharply increase at temperatures above 250°C , suggesting the presence of at least two types of active sites. The maximum amount of oxygen adsorbed is estimated to occupy $2.8\text{ m}^2/\text{g}$ or 2.6% of the total surface. Following a large number of adsorption-desorption cycles, the Graphon surface is additionally activated to yield (in part) a fraction of very active sites that are not produced at comparable burn-offs by higher temperature activation between 500 - 625°C .

9. E. Papirer, J. B. Donnet and A. Schutz, "Kinetic study of the oxidation of carbon black by ozone," *Carbon* 5, 113-25 (1967).

Three mechanisms of attack by a mixture of oxygen and ozone are distinguished depending on the type of carbon black and on the presence of moisture. Surface oxides are formed only by the treatment with dry ozone. Water is a very effective catalyst for combustion.

10. B. R. Puri, "Chemisorbed oxygen evolved as carbon dioxide and its influence on surface reactivity of carbons," *Carbon* 4, 391-400 (1966).

The combined oxygen that decomposes to evolve CO_2 (termed tentatively as CO_2 -complex) appears to play a significant role in determining surface acidity, polarity, chemisorption, heat of immersion in water, and selective adsorption from binary solutions. The removal of this complex creates unsaturated sites for the fixation of bromine.

11. B. R. Puri and R. C. Bansal, "Studies in the surface chemistry of carbon blacks, Part III. Interaction of carbon blacks and aqueous bromine," *Carbon* 3, 533-39 (1966).

The interaction involves chemical conversion to form hydrobromic acid and chemisorption of bromine. The amount of conversion varies with the surface acidity of the black, whereas the amount chemisorbed depends on how much of the CO_2 -complex was eliminated during the formation of the carbon black. Treatment with nitric acid followed by evacuation increases the bromine fixation capacity. One molecule of bromine is fixed for every two molecules of the complex eliminated. Only approximately one-half of the fixed bromine is eliminated in vacuo at 1200°C . The presence of bromine raises sorption of water, the increase being about one molecule of water per atom of bromine.

12. B. R. Puri and R. C. Bansal, "Studies in surface chemistry of carbon blacks. Part IV. Interaction of carbon blacks with gaseous chlorine," *Carbon* 5, 189-194 (1967).

Highly stable complexes with chlorine are formed at optimum temperature of 450°C . They do not decompose completely even on heating to 1200°C in vacuo but are removed almost entirely in a current of hydrogen at 800°C . The fixation of chlorine causes appreciable alteration in the water adsorption isotherm indicating changes in the pore structure, but no chemical interaction with the chlorinated surface is apparent. The heat of immersion in water increases to a small extent after chlorination.

13. B. R. Puri, C. M. Jain and R. S. Hazra, "Studies in the formation and properties of carbon-sulfur surface complexes. Part I. Formation on treatment of charcoal with carbon disulfide and hydrogen sulfide," *J. Indian. Chem. Soc.*, 43, 2, 67 (1966).

The C-S solid complex formed on treatment of sugar charcoal with H_2S or CS_2 vapor at the optimum temperature of $600^\circ C$ is highly stable. Even on outgassing at $1200^\circ C$, six percent of combined sulfur is retained. Heat treatment in a current of hydrogen results in the elimination of all sulfur as hydrogen sulfide.

14. Yu. A. Zarifyanz, V. F. Kiselev, N. N. Lezhnev and O. V. Nikitina, "Interaction of graphite fresh surfaces with different gases and vapours," *Carbon* 5, 127-135 (1967).

Adsorption isotherms and heats of adsorption of oxygen, carbon dioxide, nitrogen oxide, water, n-butane, butene-1 and isoprene have been studied on the surface of freshly cleft graphite. Low temperature oxidation studies indicate the possibility of formation of C-O-C ether bonds and of peroxide radicals. Presence of small amounts of carbon oxides in oxygen markedly exhibits the oxidation. Only approximately one percent of the sites active in adsorption on fresh graphite surfaces are free radicals as shown by ESR and magnetic susceptibility methods. Additional free radicals are formed during the interaction of these surfaces with unsaturated hydrocarbons which causes the break-up of a double bond in the adsorbate. Carbon dioxide is liberated from oxidized surfaces in vacuum between 200° and $300^\circ C$. Carbon monoxide is formed from 250° to $750^\circ C$.

C. Wetting Properties of Carbon

1. Thermodynamic Studies

1. F. E. Bartell and R. M. Suggitt, "Heat of wetting of copper, graphite, silica gel," *J. Phys. Chem.*, 58, 36-40 (1954).

Benzene, cyclohexane, p-xylene, tetralin, hexane, n-octane carbon tetrachloride, n-butanol, and methanol have positive net heats of absorption ranging from 44 to 72 erg/cm^2 . Evidence is presented that the negative heat of absorption of water (-70 erg/cm^2) is characteristic of liquid-solid systems that form contact angles. Contrary to evidence presented in other reports, presence of moisture was found to have no effect on the heats of wetting and graphite by hydrocarbons.

2. M. Belenki, W. Jouse and L. Kowalewa, "Heat of wetting of metallized carbon," *Z. Anorg. Allgem. Chem.*, 212, 362-368 (1933).

The heat of wetting by benzene of carbons metallized with Ag, Au, and Pt is given.

3. K. A. Broadbent, D. Dollimore and J. Dollimore, "The surface area of graphite calculated from adsorption isotherms and heats of wetting experiments," *Carbon* 4, 281-87 (1966).

The surface areas calculated from the vapor adsorption isotherms with methyl alcohol, isopropyl alcohol, benzene and toluene show reasonable agreement with the low temperature nitrogen values, indicating that pores which are accessible at room temperature are also accessible at low temperatures. Graphite is a suitable material for correlating adsorption and heat of wetting data.

4. R. G. Craig, J. J. Van Voorhis and F. E. Bartell, "Free energy of immersion of compressed powders with different liquids. I. Graphite powders," J. Phys. Chem., 60, 1225-30 (1956).

A method is described for the determination of the energy of wetting of a finely divided solid material which has been highly compressed into the form of plugs. The free energies of immersion of a series of different graphite powders with the liquids toluene, carbon tetrachloride, n-heptane, cyclohexane, and n-propyl alcohol were determined. The free energy of immersion is independent of the particle size of the powdered material and of pressures used in compressing the plugs; it is dependent only on the nature of the surface of the powdered material. Relative strength of absorptive bonds is calculated.

5. P. E. Berghausen, R. J. Good and W. Soller, Studies of the chemical-physical nature of adhesion, Wright Air Development Center, Report WADC-TR-56-188 (July 1956), pp. 156

In addition to the immediate heat of immersion, a slow heat of immersion is also present. The immediate heat of immersion is associated with the Van der Waals forces of attraction across a solid-liquid interface. The slow heat of immersion is postulated to be the result of chemical reactions between the immersing liquid and the solid. In the case of Graphon, surface oxidation by water with the formation of a surface C-O complex is postulated to be the cause of the slow heat.

6. J. J. Chessick, A. C. Zettlemoyer and Yung-Fang Yu. "Free energies, heats and entropies of wetting of graphite," J. Phys. Chem., 64, 530-531 (1960).

The heats of monolayer formation of toluene, carbon tetrachloride, n-heptane, cyclohexane, and 1-propanol on graphite were determined and entropies of monolayer formation were calculated. Serious difficulties arose in interpretation, since the results cannot be explained on the basis of customary adsorption thermodynamics.

7. R. J. Good, A. Girifalco and G. Kraus, "A theory for estimation of interfacial energies. II. Application to surface thermodynamics of teflon and graphite," J. Phys. Chem., 62, 1418-21 (1958).

For graphite, the total surface energy is estimated to be 119 erg/cm², the surface free energy 70 erg/cm², and the surface entropy 0.16 erg/cm² deg.

8. "Forces in detergency, Part II," in Soap and chem. spec., 37, 50-2 (June, 1961).

The article compares heats of wetting of graphite, charcoal, and Graphon with other powdered solids.

9. F. H. Healey, "The heats of immersionsal wetting of rutile and Graphon in organic liquids," J. Phys. Chem., 58, 887-90 (1954).

The heats of immersion have been measured in water and in a series of organic liquids differing in functional group, chain length, or chain branching. The heat values for rutile were found to depend upon the functionality of the wetting liquid; however, except for water, the values for Graphon were almost the same for all the liquids.

10. F. H. Healey, Yung-Fang Yu, and J. J. Chessick, "The detection of hydrophilic heterogeneities on a carbon surface," J. Phys. Chem., 59, 399-402 (1955).

The effect of increasing the amount of surface oxide on Graphon on both the water vapor adsorption isotherms and the heat of immersion in water was studied. The ratio of the apparent area available to water adsorption to the total area of Graphon determined by nitrogen adsorption was taken as a measure of the fraction of oxidized surface. Degassing caused a considerable decrease in the number of hydrophilic sites due to volatilization of oxygen complexes on the surface of the original sample. The heat of immersion in water did not prove to be a linear function of the fraction of hydrophilic surface. The increasing slope of the heat of immersion vs. hydrophilic fraction appeared to indicate that the interactions between molecules adsorbed on adjacent patches of oxide sites increased with the increasing number of patches on the surface. The slope and intercept of the curve for the more hydrophobic samples was used to estimate the heat of wetting of the carbon surface and of the hydrophilic sites.

11. Gerard Kraus, "The heat of immersion of carbon black in water, methanol and n-hexane," J. Phys. Chem., 59, 343-5 (1955).

Heats of immersion have been measured on nine carbon blacks in water, methanol and n-hexane. The heats of immersion in the two polar, hydrogen bonding liquids are shown to be approximately linear functions of the oxygen content per unit surface area of the black, indicating that virtually all the oxygen in carbon black is present in the form of a surface complex. The heats of immersion in n-hexane are nearly constant for all carbon blacks. Removal of active sites by graphitization does not materially alter the overall interaction energy between carbon black and nonpolar adsorbates. This result is interpreted as evidence for an accompanying loss of low energy sites in passing from the heterogeneous carbon black surface to the homogeneous surface of Graphon.

12. C. Pierce and John Mooi, "Heats of wetting for carbon blacks," Abstracts of papers, 130th meeting, Amer. Chem. Soc., 121 No. 28. (1956).

Heats of wetting in benzene are determined for Graphon and various carbon blacks, as a function of the amount of vapor preadsorbed. Differential heats of adsorption are computed from the heats of wetting. A critical study is made of the comparative merits of this method and direct measurements of heats of adsorption.

13. B. R. Puri, "Chemisorbed oxygen evolved as carbon dioxide and its influence on surface reactivity of carbons," Carbon 4, 391-400 (1966).

The combined oxygen that decomposes to evolve carbon dioxide (termed tentatively as CO_2 -complexes) appears to play a significant role in determining surface acidity, polarity, chemisorption of water and methanol, heat of immersion in water, and selective adsorption from binary solutions. The removal of this complex creates unsaturated sites for the fixation of bromine: one molecule of bromine is fixed for every two molecules of the complex eliminated.

14. B. R. Puri, P. C. Gupta, and M. L. Lakhanpal. "Heat of wetting of charcoal by water," J. Indian Chem. Soc., 31, 435-8 (1954).

Integral and differential heats of wetting of five different varieties of charcoal were determined calorimetrically. The heat of wetting by a monolayer of water was a little more than twice the heat of fusion of ice in the case of every sample. The heat of wetting was almost negligible when the charcoal was equilibrated with air 70 percent relative humidity.

15. B. Puri, D. D. Singh, and L. R. Sharma, "The heat of immersion of charcoal as a function of its oxygen complexes," J. Phys. Chem., 62, 756-58 (1958).

Heats of immersion of methyl alcohol, ethyl alcohol, n-hexane, and benzene are independent of the chemisorbed oxygen, whereas the immersional heat of water is a function of that portion of surface oxide which desorbs as CO_2 .

16. F. I. Razour, Sh. Nashed, and W. E. Mourad, "The heats of wetting of carbons in relation to their specific surface areas," Carbon 2, 359-64 (1965).

No simple correlation was found between the heats of wetting in methanol of a number of carbons and the specific surface areas of the carbons calculated from the adsorption isotherms of methanol vapor.

17. N. Rice, "Heats of wetting of carbons prepared from low rank coals," Proceedings of the 4th Carbon Conference, 1959, Buffalo Univ., pp. 23-27.

The coals from which these chars were derived were of sub-bituminous rank. Relationships between density, void space, and heats of wetting in methanol are discussed.

18. A. C. Zettlemoyer, "Immersional wetting of solid surfaces," Chemistry and physics of interfaces, Amer. Chem. Soc. Symposium, 1964, pp. 138-48. Originally published in Ind. Eng. Chem., 57, 26-36 (1965).

Includes heat of immersion values for various solids, including graphite, in water, benzene, and other liquids.

C. Wetting Properties of Carbon

2. Contact Angle Studies

1. R. W. Bartlett and J. K. Hall, "Wetting of several solids of Al_2O_3 and BeO liquids," Amer. Ceram. Soc. Bull., 44, 444-48 (1965).

The high contact angles in conjunction with the high chemical reactivity caused severe pitting of the graphite.

2. J. Benak and T. B. Selover, Jr., "Wettability of graphite by barium fluoride-calcium fluoride eutectic," Eighth Biennial Conference on Carbon, Buffalo, New York, June 19-23, 1967, Section C 138.

Change from non-wetting ($\theta > 90^\circ$) to wetting ($\theta < 90^\circ$) takes place at a surface tension of the melt of approximately 190 dynes/cm.

3. D. J. Brown, V. R. Gray, and A. W. Jackson, "The spreading of oil on wet coal," J. Appl. Chem., 8, 752-9 (1958).

The spreading of oil on wet coal is shown theoretically to depend on two factors: the water/oil/coal contact angle and the oil/water interfacial tension. From these factors, two criteria of spreading can be derived: the "spreading coefficient" and the "adhesion tension" relating to spreading on flat surfaces and spreading into capillaries, respectively.

4. H. Dawe and R. F. Stevens, "Alteration of surface characteristics of graphite by adsorbed gases," Proceedings of 4th Carbon Conference, Buffalo Univ., pp. 17-20 (1959).

The use of air and ozone at elevated temperatures resulted in the most hydrophilic nature for graphite powder.

5. A. R. Ford and A. E. White, "The use of graphite at high temperatures," Trans. Inst. Chem. Engrs., 41, Section CE61-68 (No. 2, 1963).

Contact angles of Hg and molten Ag, Au, Ni, Fe, Si, Zr, MoO_3 , V_2O_5 , B_2O_3 , and of several glasses on different types of graphite are given. Fe, Si, Zr, and the oxides are good wetters.

6. R. Eissler, "Contact angle studies on surfaces of coal and on other surfaces of low free energy," PhD thesis, University of Illinois (1960) No. 60-1638.

Advancing and receding angles of a series of polar liquids were measured on faces and edges of naphthalene crystals, graphite leaflets, and a series of coals of varying rank. Naphthalene edges were found to be slightly less wettable by the liquids than naphthalene faces, whereas, the reverse was true for graphite. Contact angles measured on coals showed large hysteresis. Specific surface tensions for graphite face and graphite edge are 42.0 and 44.0 dynes/cm, respectively.

7. R. L. Eissler, and K. E. Van Holde, "Wettability of coal, graphite, and naphthalene as measured by contact angles," Illinois State Geological Survey. Circular 333, pp. 20 (1962).

A condensed version of the R. L. Eissler PhD thesis.

8. S. A. Ershova, L. G. Povedskaya, and V. N. Chernyaev, "Wettability of graphite and quartz with zinc and antimony," *Tsvetn. Metal.*, 37, 83 (No. 6, 1964).

Poor wettability is improved somewhat at reduced pressures.

9. P. J. Kreyger and S. S. Kirslis, "Sessile drops of molten halides on graphite and metals," Oak Ridge National Laboratory, NSA 18, 23437 (Jan. 23, 1964).

Molten KCl and NaCl-NCl mixture wet the graphite and the metals in the sense that the contact angle was smaller than 90°C. Molten fluorides with a high surface tension, e. g., Li_2BeF_4 and LiF-NaF, did not wet the graphite, or metals free of surface oxides. Wetting of graphite by beryllium containing molten fluorides occurred when small amounts of water vapor (10 ppm) were present in the gas phase, resulting in the permeation by salt of the porous graphite.

10. O. G. Ingles, "The contact angle of mercury at coal and char surfaces," *Fuel*, 36, 252-4 (1957).

It is shown that the generally accepted value of 140° for the advancing contact angle of mercury on carbon surfaces does not apply in the porosimetry of many coals and chars.

11. R. Kieffer, H. Nowotny, and S. Windisch, "On novel types of tantalum-niobium infiltrated or sintered alloys and compound materials with graphite," in Plansee Proc., 1964 Benesovsky, Ed., pp. 486-510. Trans. LATR-64-27.

Wetting of graphite with CuSi and MoSi alloys; C-TaC, C-TaC-Ag(Cu); C-W-Ag(Cu), TaC-Ag(Cu) alloy systems; infiltration of NbC-Ta-C, Mo, W, and Re into graphite are discussed.

12. G. K. Moiseev and G. K. Stepanov, "Surface wetting of some materials by molten carbonates of alkali metals," Electrochem. of molten and solid electrolytes, V. 5, Ural SSSR Acad. Sci., pp. 101-9.

Includes data on BN, graphite, Pt, Pd, Ag, Ni, and Zr in CO_2 , H_2 and He atmospheres.

13. Yu. V. Nadich and G. A. Kolesnichenko, "Wetting of graphite and diamond by molten metals and alloys," *Poroshkovaya Met.*, Akad. Nauk Ukr. SSR 1, No. 6, 55-62 (1961).

The wetting of graphite by Cu, Ag, Ge, Sn, In, Si, Al, Bi, Pb, Ni, Co, Fe, Pd, Sb, Ti, Cr, V, Nb, and their alloys with Cu, was studied. Transition metals, as a rule, wet graphite well. Only Al and

Si among the nontransition metals wet graphite because they form stable carbides. Chemical reaction and participation of unfilled electron d-shells of metal atoms played a considerable part in wetting. Pure Ni, Co, Fe, and Pd wet graphite well.

14. Y. V. Naidich and G. A. Kolesnichenko, "Investigation of wetting of diamonds and graphite by liquid metals , II. " Poroshkovaya Met., No. 1, 1963, pp. 49-53. Translated in Sov. Powder Metal, No 1, 35-38 (Jan. - Feb. 1963),

A study of the effect of concentration and temperature on the angle of contact between graphite and liquid copper and tin titanium alloys by the sessile drop method in temperature range 800-1150° at 10^{-5} mm Hg.

15. Y. V. Naidich and G. A. Kolesnichenko, "Investigation of the wetting of diamond and graphite by fused metals and alloys, " Porosh. Met. No. 3, 1964, pp. 23-28.

Contains data on contact angles of Cu, Ag, Au, Ge, Sn, In, Sb, Pb, Al, Ti, and Cr; of B alloyed with Cu, Sn, and Ag; also data on the wetting by the alloys Cu-Cr, Cu-Ti, Sn-T, and Cu-Su-Ti. The principles governing the wetting of graphite and their applicability of diamond are discussed.

16. Y. V. Naidich and G. A. Kolesnichenko, "Investigation of wetting of diamond and graphite by fused metals and alloys, " Porosh. Met. No. 2, 1966, pp. 97-99.

The molar work of adhesion of the investigated liquid Cu, Ga, In, and Pb to diamond and graphite is small and equals 0.6-2 kcal/mol with practically no temperature variation. Interaction is attributed to the Van der Waals forces.

17. A. M. Saul, et al., "Behavior of rocket nozzle materials at high temperatures and pressures of combustion product gas mixtures, Aeronutronic (Final Technical Report), (Dec. 15, 1963), NOw 61-0905-c, Task D, ARPA Order No. 22-62.

Contact angles of molten Al_2O_3 and BeO on graphite are greater than 90°. A severe drop pitting of the graphite surface occurred.

18. W. F. Witzke, "The adhesion of molten boron oxide to various materials, " RM E57L11 (Apr. 1, 1958) (AD156-392) U60-4-5: 202. National Advisory Committee for Aeronautics.

Graphite is poorly wetted by boron oxide, the contact angle remaining above 100 degrees. At 1100°C, the work of adhesion for the boron oxide-graphite interaction is 48 dynes per centimeter. This value is half that for the boron oxide-boron nitride interaction and approximately one-third of that for the boron oxide-metal interaction.

D. Adsorption Properties of Carbon

1. A. C. Zettlemoyer and K. S. Narayan, "Adsorption from solutions by graphite surfaces," Chemistry and Physics of Carbons, Vol. II, Philip L. Walker, Jr., Ed., Marcel Dekker, New York, 1966, pp. 197-224. A good review of this field is given in Reference 1. (60 References)

The emphasis is on the thermodynamic aspects of the interfacial films formed on graphite (mainly Graphon with hydrophobic surface of $100 \text{ m}^2/\text{g}$ and a medium surface energy 110 ergs/cm^2) from solutions of simple organic compounds with varying degrees of polarity and zwitterion character (amino acids).

2. F. E. Bartell and E. J. Miller, "Adsorption of activated sugar charcoal, I." *J. Amer. Chem. Soc.*, 44, 1866-80 (1922).

Adsorption of methylene blue, a basic dye of the electrolyte type, by activated, ash-free sugar charcoal has been studied. This adsorption is partially, if not entirely, hydrolytic in nature.

3. F. E. Bartell and E. J. Miller, "Adsorption of activated sugar charcoal, II." *J. Amer. Chem. Soc.*, 45, 1106-15 (1923).

The adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali, which remains in solution. The introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending upon the nature of the acid, whereas, the introduction of the amino group decreases the adsorption of the acid. The effect of the amino group is considerably greater than that of the hydroxyl group.

4. R. Burstein and A. Frumkin, "On the behavior of out-gassed activated carbon in electrolytes," *Z. Physik. Chem.*, A 141, 219-220 (1929).

Sugar charcoal outgassed at 1000°C and 10^{-6} mm Hg does not show any electrolytic adsorption but contains only an electric double layer. After exposure to air, it becomes positively charged and begins to adsorb acids.

5. H. R. Kruyt and G. S. de Kadt, "Charge on carbon," *Kolloid Z.* 47, 44 (1929).

Ash-free adsorption carbons have a negative charge. After they are heated to 100°C in an atmosphere of carbon dioxide or in vacuum, these carbons acquire a positive charge in water. This positive carbon, however, regains its negative charge against pure water if the carbon is heated to 400°C in a stream of oxygen.

6. D. Rivin, "Hydride-transfer reactions of carbon black," American Carbon Committee Carbon Conf., 5th Proc., p. 199-210 (1961).

Cationic surface sites have been identified on both production and vacuum heat-treated carbon blacks, after the blacks are oxidized in the presence of acid. Reduction of the electron deficient (oxidized) carbon surface by hydride transfer mechanisms is described. The apparent stability of charged surface structures is attributed to aromatic resonance in the graphite layer planes of microcrystalline carbons.

7. D. Villars, "Studies on carbon black; I. Electrometric titration," J. Amer. Chem. Soc., 69, 214-217 (1947).

A number of neighboring empty spaces greater than unity is required before H^+ ion can adhere to the carbon black surface. This number increases with the oxygen content of the carbon. The system behaves as if presence of oxygen on the surface increases the free space required by hydrogen ions before they can successfully adhere to the surface.

8. B. Steenberg, Uppsala, Almqvist and Wiksells Boktryckerik Aktiebolag, Adsorption and exchange of ions on activated charcoal, In English. p. 193 (1944).

The applicability of the Donnan theory to the adsorption of electrolytes on gas activated charcoal is assumed in order to present a theory of hydrolytic adsorption. The phenomena included under this term are interpreted as analogues of the so-called Donnan hydrolysis. It is shown that all observations concerning the hydrolytic adsorption in inorganic and organic salts on charcoal may be interpreted with ease in accordance with this theory.

9. Elroy J. Miller, "Adsorption of electrolytes by ash-free charcoal. VII," J. Phys. Chem., 36, 2967-86 (1932).

Brief survey of the present status of the subject, and evidence that negative adsorption of inorganic bases decreases with length of time of contact of charcoal with solution.

A brief survey of the recent trends and developments in studies on adsorption of electrolytes by ash-free charcoal is presented. No single theory seems capable of explaining satisfactorily all the known facts of adsorption of electrolytes by adsorbent charcoal.

E. Literature Related to Surface Properties of Carbon Fibers

1. D. V. Bademi, J. C. Joiner, G. A. Jones, "Microstructure of high strength, high modulus carbon fibers," Nature, 215, 386-7 (1967).

Transmission electron micrographs, replicas and cut ends of the fibers indicate that the fibers are composed of fibrils running parallel to the fiber axis.

2. Battelle Memorial Institute, Development of filament reinforced metals, Final Report, (Jan. 1967), Contract NOw 65-0615-c, (1967).

Electroless coatings of pure nickel, cobalt, and platinum were produced on "Thornel" 25 yarn through the use of hydrazine as reducing agent. Metal-coated "Thornel" filaments were of limited value for preliminary property evaluations because of the poor metal-filament bond and because of the tendency for the coatings to agglomerate on heating due to the limited wetting of graphite by the metal.

3. P. W. Harruff and S. A. Moorefield, "Processing considerations for composites for graphite fibers and polyimide resins," Advances in Structural Composites, Soc. of Aerospace Material and Process Engineers, Volume 12, 1967, Section 9-2.

Removal of PVA size from "Thornel" 40 by heat cleaning at 600°C in nitrogen atmosphere improves composite properties with polyimide, epoxy, phenolic, and diphenyloxide resins.

4. J. W. Herrick, "Graphite fiber reinforced epoxy composites," Advances in Structural Composites, Soc. of Aerospace Material and Process Engineers, Volume 12, 1967 Section AC8.

The flexural strength of "Thornel" 25 composites was increased twofold by boiling the fibers in 60 percent nitric acid for 24 hours. Other surface treatments, such as air oxidation at 500°C, boiling in acetone, nickel coating, nylon coating, or heating to 300°C followed by vacuum impregnation, did not significantly improve the composite shear strength.

5. J. W. Herrick, Surface treatments for fibrous carbon reinforcements, Part I and II, Technical Report AFML-TR-66-178, Part I (July 1966) and AFML-TR-66-178, Part II (June 1967).

Detailed discussion of the work reported in Ref. 5 Chemical functionality was much more important in determining the interlaminar shear strength than was the surface area, which can be increased by nitric acid treatment of "Thornel" 25 from 1-2 m²/g to about 12 m²/g.

6. W. Johnson and W. Watt, "Structure of high modulus carbon fibers," Nature, 215, 384-6 (1967).

The X-ray studies on carbon fiber with a Young's modulus of $60 \cdot 10^6$ lb/in.² derived from polyacrylonitrile show turbostratic crystalline structure with L_c of at least twelve layer planes and L_a in the range of 60-120 Å. Electron microscopy revealed a highly oriented fibrillar structure.

7. D. W. Marshall, "The effect of certain resin and surface variables on the interlaminar lap shear strength of carbon cloth composites," Advances in Structural Composites, Soc. of Aerospace Material and Process Engineers, Vol. 12, Section P-7.

Oxidizing the surface of carbon cloth by immersion in potassium permanganate solution results in a slight increase in lap shear strength; treating with phosphoric acid increases the oxidation resistance but decreases the lap shear strength. Heating of carbon cloth under vacuum prior to coating with resin results in a decrease in lap shear strength.

8. B. K. Morse, Graphite fibers as reinforcements in a metal matrix. A definition and discussion of the problem. Technical Report AFML-TR-66-346- (December 1966).

Thermodynamic principles of chemical inertness and thermal stability were explored to develop a theory and definition of the model composite. The concept of "mutual insolubility" of the two elements at the melting point provides a criterion for both chemical inertness and the range of thermal stability. This concept was applied to predict possible metal matrices and/or coatings for graphite fibers. The concepts of the surface free energy of graphite and metals are discussed in order to clarify the fabrication difficulties.

Seven possible binary systems and twelve ternary systems may be considered for use with graphite over a wide temperature range. Except for nickel, none of the metals is considered suitable for use as a structural material.

9. S. P. Prosen and R. Simon, "Shear strength improved 300 percent in graphite fiber composites," Reinforced Plastics and Comp. World 6, 30 (1967).

This result was obtained by depositing SiC whiskers on graphite filaments in a basic hydrogen atmosphere at 1100-1650°C.

10. R. Simon, S. P. Prosen, and J. Duffy, "Carbon fiber composites," Nature, 213, 1113-4 (1967).

Polyacrylonitrile derived carbon fibers show inverse behavior of the interlaminar shear strength with the Young's modulus in epoxy matrix composites. This result cannot be attributed directly to poor wetting, since the critical surface tension fibers with a modulus of $68 \cdot 10^6$ lb/in.² is between 44-48 dyne/cm, a value which is greater than that of the surface energy of most epoxy resins. Spontaneous wetting, therefore, should and does occur.

11. Union Carbide Corporation, Carbon Products Division, Integrated research on carbon composite materials, Technical Report AFML-TR-66-310. Part I. (1966).

Methods are developed for contact angle measurements on individual graphite fiber filaments and for the determination of wicking rates in order to study the effects of surface treatments.

12. Union Carbide Corporation, Carbon Products Division, High strength-high modulus carbon fibers, Technical Report AFML-TR-66-334, Part I. (1966).

Section II of this report (pp. 58-59) on morphology contains much information on the internal structure of low modulus carbon fibers obtained by X-rays as well as the results of transmission and replication electron microscopy on carbon, graphite, and "Thornel" yarns.

13. R. Sprague, "Serial replication of selected areas of carbon fibers," Abstract of a paper presented at the 24th Annual Meeting of the Electron Microscopy Society of Science, J. Applied. Phys., 37, 3923 (1966).

Handling techniques of 10 μ diameter carbon fibers are described in order to assure the replication of the same area before and after surface treatment.

14. United Aircraft Corporation, Investigation of physical and chemical nature of the surface of recently developed fibers, Technical Report AFML-TR-218, Part I. (July 1967).

Electron microbeam probe analysis indicated that significant surface contamination of yarn by oxygen occurs during longer Soxhlet extraction of graphite yarn with water to remove polyvinyl alcohol. The surface area of "as received" "Thornel" 25 fiber was found to be a $.8 \pm .1 \text{ m}^2/\text{g}$. A technique based on gas chromatographic retention times was evaluated to determine the affinity of different compounds with specific functionality for graphite yarn.

Section III

EXPERIMENTAL STUDIES OF PHYSICAL SURFACE PROPERTIES OF CARBON AND GRAPHITE FIBERS

This study was undertaken mainly to determine the surface properties of "Thornel" 40, which, at the time of this work, represented the most advanced form of commercially available carbon fiber with high modulus continuous filaments. "Thornel" 50 was developed too late to be included in this report. Surface properties of other types of carbon fiber were interesting for the purpose of comparing their behavior in composite materials in so far as the surface might have an effect on the composites. Work with "Thornel" 40 yarn which had been etched with chromic acid solution is also reported because of previous findings that such treatment improved the compressive strength of graphite fiber-epoxy in the NOL ring test.¹

A. Experimental

Mercury density, mercury pore distribution (0.02-100 microns), nitrogen pore distribution (0-600Å), and surface area were determined on 16 samples of carbon and graphite yarns. The 16 samples included the following yarns: one low-modulus carbon yarn, lot 602137-5; one "Thornel" 25 yarn, lot 03107T-3; four low modulus graphite yarns, two each from lot 603097 and lot 203167-2; eight "Thornel" 40 yarns, two each from lots 03107T-4 and S-504307-1 and four from lot 03107T-5; and one sample of "Thornel" 40, lot 03107T-5, which has been treated with cleaning solution.

All samples with the exception of one were prepared in our standard production facility; lot No. S-504307-1 was made in an experimental facility. All yarn samples were prepared with water finish. During the preparation of the samples for surface measurement, which involves outgassing at 400°C in high vacuum, small amounts of volatile, tar-like substances evolved from the standard production samples. This observation indicated the possibility of slight contamination with PVA, caused by incomplete purging of the finish applicator with water. In order to eliminate danger of partial carbonization of this residual material during the heat-cleaning cycle, which might affect the surface area and the pore size distribution, all of these samples have been washed by Soxhlet extraction with distilled water for 6 hours. After this treatment, the amount of volatiles was negligible. Samples from lot S-504307-1 did not require any washing.

For statistical purposes, at least two samples were to be run of each type and/or lot of fiber; however, because of insufficient quantity of "Thornel" 25 and the very long experimental time (about 20 days)

needed to obtain data on low modulus carbon yarns, only one sample of each was run. The purpose for running several lots on some of the yarns was to check lot-to-lot variation. In addition, variations within a lot and variations in the testing procedures were checked by running four separate samples of the same lot.

Mercury pore distributions and mercury densities were determined by means of Aminco-Winslow Model 5-7109 Porosimeter, equipped with a standard 6cc penetrometer, from mercury intrusion data obtained on yarn samples dried overnight at 120°C. The intrusion data were corrected for compressibility of mercury head pressure, and barometric pressure and smoothed by least squares techniques.

Nitrogen pore distributions and surface area were determined on samples which had been dried overnight at 120°C. The sample size chosen, whenever possible, was approximately 25 grams. The instruments used to determine the sorption isotherms (a plot of volume of nitrogen sorbed versus the ratio of the pressure of the nitrogen upon the sample to the vapor pressure of nitrogen) were fabricated "in house" and are not available commercially. The surface area was calculated from the adsorption isotherm in the partial pressure range of .05 to .15 through the use of the BET equation.² The Barrett, Joyner and Halenda method³ as modified by Roberts⁴ was used to calculate the pore distributions from the desorption isotherm.

B. Results and Discussion of Mercury Intrusion Data

The results of the mercury pore distributions were rather disappointing. The packing of the yarn fiber into the penetrometer (device to hold the sample during test) creates "pseudo-pores." These "pseudo-pores" are not reproducible and constitute the largest volume of pores measured in the test. Consequently, no useful information was obtained from the mercury intrusion method except for the mercury density (bulk density with all pores greater than 0.02 micron filled). The values for the mercury densities are given in Table III in Section IVC. A steady increase in fiber density occurs as graphite is processed into "Thornel" 25 and then into "Thornel" 40. This result is probably due to a reduction in the number of small pores which the mercury cannot penetrate and to an increase in the order of the structure as graphite is processed into "Thornel" 40. The mercury density of the carbon fibers is nearly as great as that for "Thornel" 40 (1.52 versus 1.59 g/cc). This apparently high density of the carbon fiber is probably caused by the destruction of the pore structure of the carbon yarn under the test conditions, whereas the graphitized yarns are capable of maintaining their structures under the conditions of the test.

C. Results and Discussion of Nitrogen Sorption Data

Generally, the determination of surface area by the BET method is considered to be accurate within approximately 10 percent and to be reproducible within approximately 3 percent for "normally behaved" $5 \text{ m}^2/\text{g}$ or higher surface area samples. Carbon yarns do not "behave normally," and the accuracy of the surface area measurement is not known. Although the graphitic yarns are "behaved normally" their very low surface area ($\sim 1 \text{ m}^2/\text{g}$) causes difficulty in the determination of their surface area accurately and reproducibly. The reproducibility and accuracy of nitrogen pore distributions has not been established. In order to estimate the reproducibility of our measurements and the consistency of a given lot of "Thornel" 40, the surface areas and pore distributions of four separate samples of the same lot of "Thornel" 40 were measured. The results which are tabulated in Table I are very satisfying. A typical sorption isotherm for these samples is shown in Figure 1, a typical BET plot in Figure 2, and a typical pore distribution in Figure 3.

In order to study variations between the lots, three separate lots of "Thornel" 40 and two different lots of graphite fibers were run. The results are tabulated in Table II. Two of the "Thornel" 40 lots agree very closely; a third differs somewhat, but not greatly from the other two lots. The two graphite lots are in good agreement, except that the surface area is approximately 50 percent higher in one of the lots. Measurements of materials with very low surface areas are difficult because very minor changes in the small pores can greatly affect the total surface area.

The results obtained from measurements of all four types of fibers are tabulated in Table III. Whenever possible, the value is followed by its standard deviation, or, when only two runs were made, by the average deviation so that we may have an estimate of the precision of the test. For those samples for which only one run was made, our experience indicates that the precision of measurement will be approximately the same as that which occurs for the other yarns. The surface area of $1.6 \text{ m}^2/\text{g}$ for "Thornel" 25 is different from the $4 \text{ m}^2/\text{g}$ reported in Union Carbide Technical Information Bulletin No. 465-201 IF. The latter value, which was obtained on some of the very first "Thornel" 25 samples, must now be considered too high, particularly since the independent determinations by J. S. Herrick (see: Bibliography, Section V, Ref. 6 Part II) finds the value of $1-2 \text{ m}^2/\text{g}$ while the value of $0.8 \pm .1 \text{ m}^2/\text{g}$ quoted by the United Aircraft Corporation (see: Bibliography, Section V, Ref. 16) seems to be too low in the light of our very reliable data on "Thornel" 40.

TABLE I
ILLUSTRATION OF PRECISION OF POROSITY AND
SURFACE AREA MEASUREMENTS BY NITROGEN SORPTION TEST*

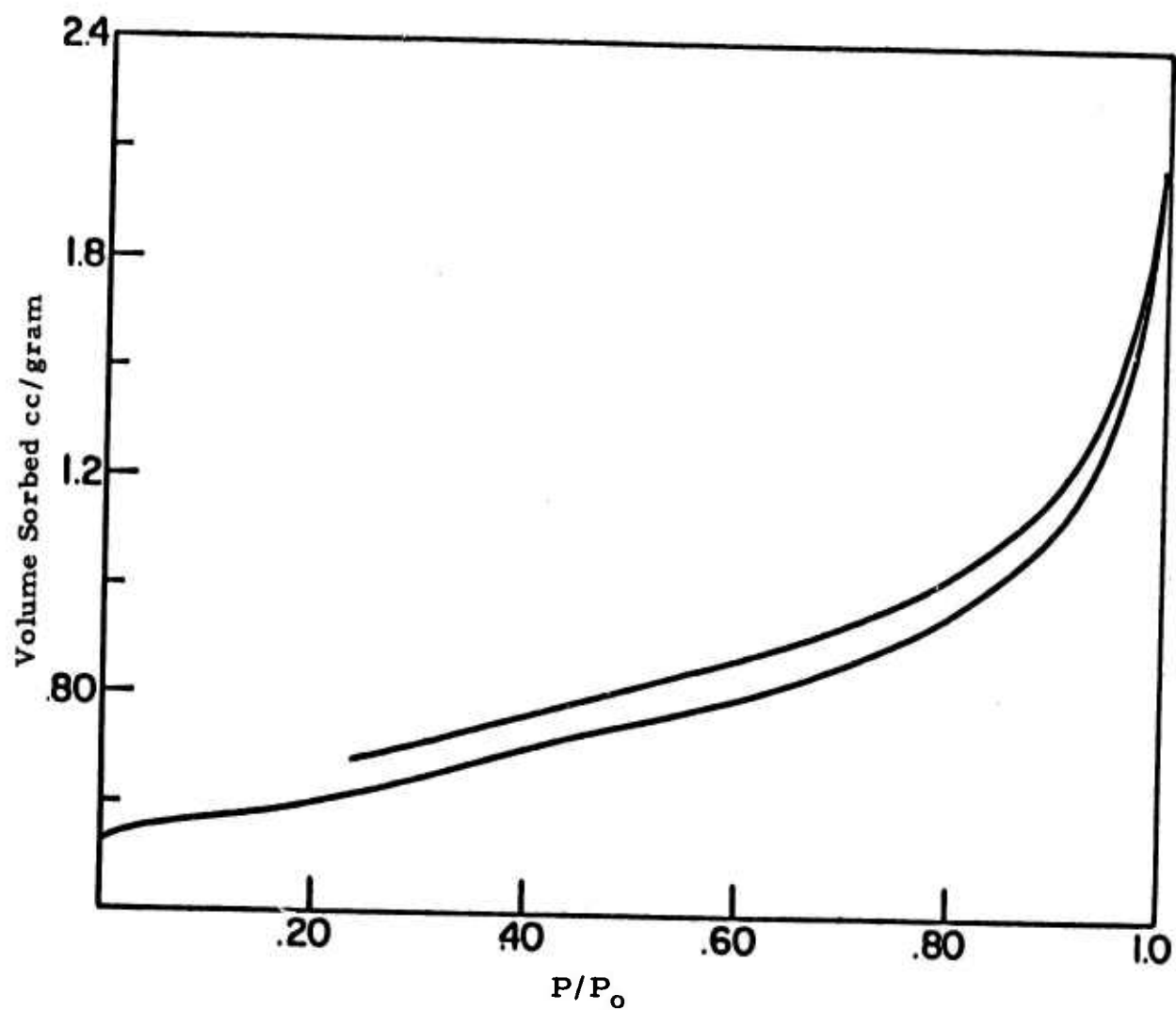
	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter, Angstrom		
			Upper Quartile ¹	Median ²	Lower Quartile ³
Run 1	1.3	.0033	550	170	62
" 2	1.4	.0030	375	135	57
" 3	1.6	.0031	375	135	53
" 4	1.2	.0029	475	135	57
Mean	1.38	.00306	444	144	57
Standard Deviation	.17	.00017	85	18	3.6
Coefficient of Variation (%)	12	6	19	13	6

*Based on "Thornel" 40 lot 03107T-5

¹ 25 percent of the total pore volume is contained in pores with diameters larger than the values shown in this column

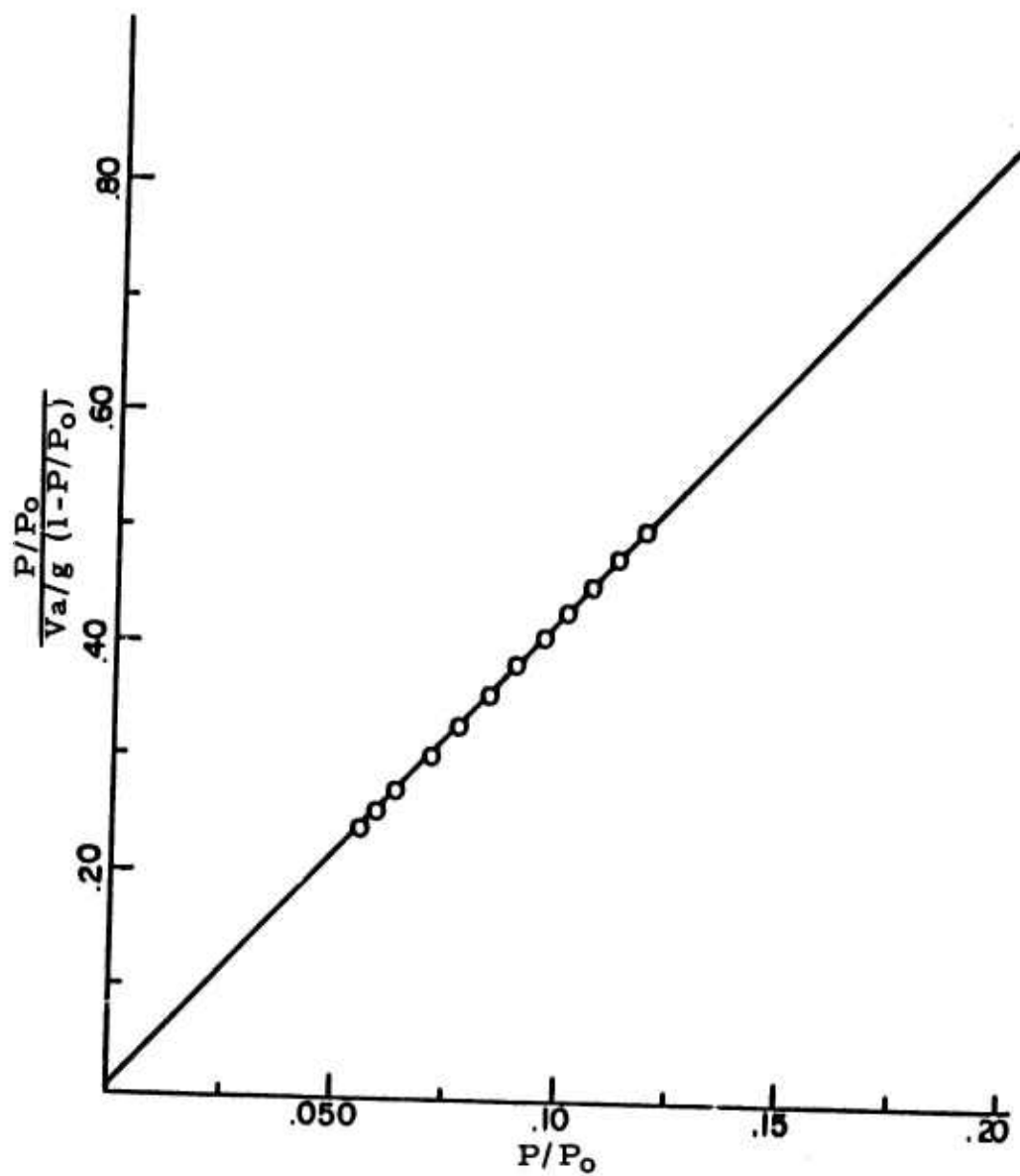
² ditto for 50 percent of the total pore volume

³ ditto for 75 percent of the total pore volume



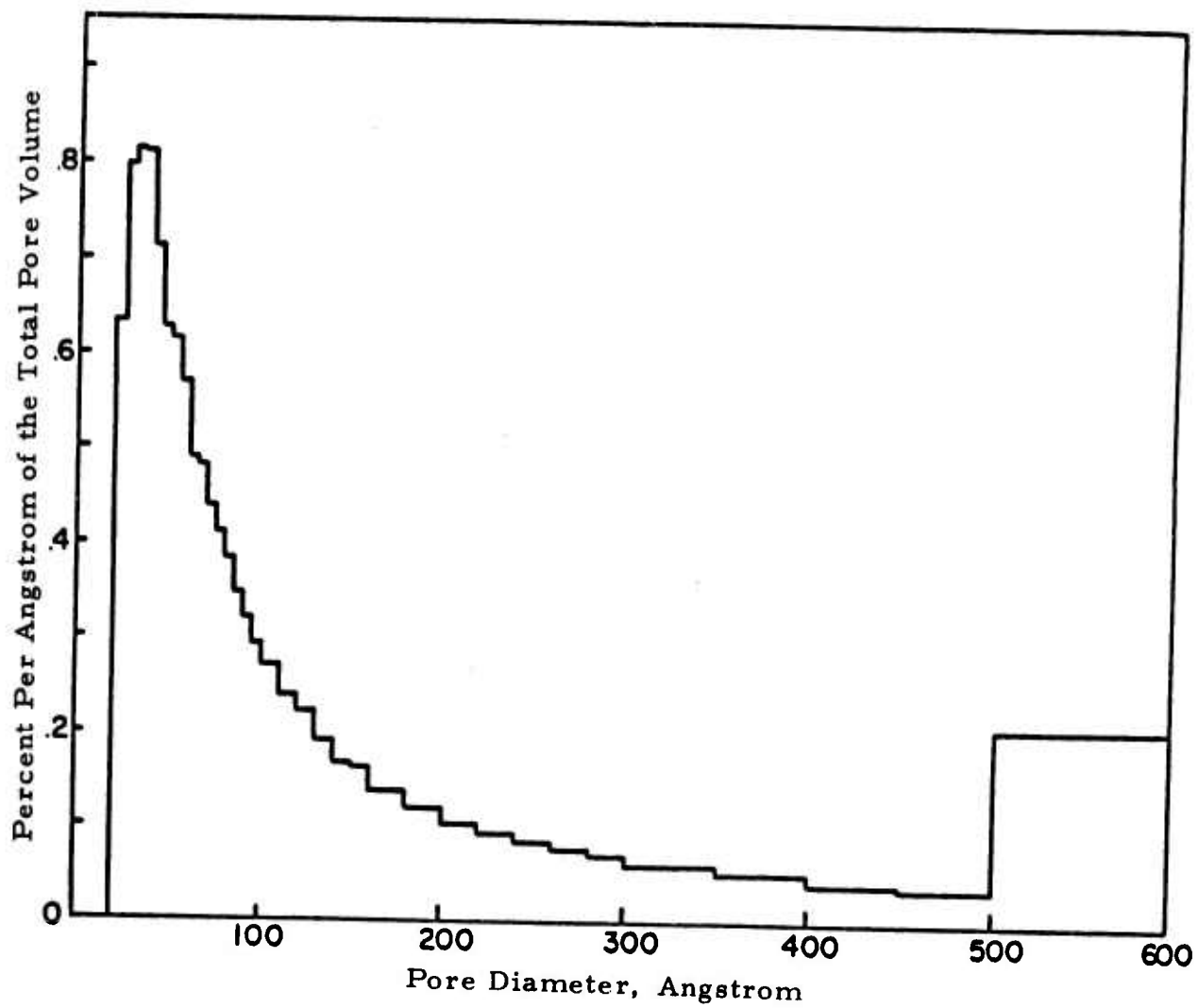
N-18064

Figure 1. Typical Sorption Isotherm for "Thornel" 40



N-18065

Figure 2. Typical BET Surface Area Plot for "Thornel" 40



N-18068

Figure 3. Typical Pore Distribution for "Thornel" 40

TABLE II
VARIATION OF POROSITY AND SURFACE AREA AMONG LOTS

Yarn	Lot	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter, Angstrom		
				Upper Quartile *	Median	Lower Quartile
"Thornel" 40	03107T-5	1. 38	. 00306	444	144	57
"Thornel" 40	03107T-4	1. 35	. 00320	450	135	57
"Thornel" 40	S-504307-1	1. 05	. 00273	550	260	94
Graphite	203167-2	1. 45	. 00245	280	101	50
Graphite	603097	1. 00	. 00266	325	115	53

* For explanation see Table I

TABLE III
SUMMARY OF POROSITY DATA ON FIBERS

	Total Pore Volume cc/g (0-600Å)	Surface Area (m ² /g)	Pore Diameter, 0-600 Å			Mercury** Density (0. 2μ) g/cc
			Upper*** Quartile	Median	Lower Quartile	
Carbon*	. 129	281	all pores less than 20 angstroms			1. 52 ± . 03
Graphite	. 0025 ± . 0002	1. 3 ± . 4	295 ± 28	106 ± 9	51 ± 3	1. 28 ± . 01
"Thornel" 25*	. 0033	1. 6	475	155	63	1. 46 ± . 05
"Thornel" 40	. 0030 ± . 0002	1. 3 ± . 2	473 ± 75	166 ± 59	67 ± 18	1. 59 ± . 02

* Based on one run only

** Based on pairs of runs

*** For explanation see Table I

The geometric surface areas of "Thornel" 25 and "Thornel" 40 are 0.57 m²/g and 0.56 m²/g, respectively.⁵ These calculated surface areas, considered together with only slightly higher total pore volume and with almost identical pore size distribution, indicate that the surface area of "Thornel" 25 should be very little above that for "Thornel" 40; this study confirms this prediction (see Table III).

D. Electron Micrographs of Carbon Fibers

Surface replicas of all fibers included in this report are shown in Figures 4 to 9. The strips of five pictures, in the magnification range from 6000 to 20,000, show different areas representative of surface features typical for each lot. In general, carbon fibers are distinguished by lack of surface detail; the graphite fibers show well developed surface roughness and the "Thornel" fibers are characterized by a high degree of orientation of the striations of the surface which are, perhaps, less perfectly developed in "Thornel" 25 than in "Thornel" 40. These differences are even more accentuated in the higher magnifications shown in Figures 10 through 13.

It is interesting to consider the experimental sample S-504307-1 in the light of the pronounced surface heterogeneities revealed in the electron micrographs. This yarn could be considered as being nominally "Thornel" 40, except for unusually low tensile strength and exceptionally large standard deviations in both tensile strength and Young's modulus (see Table IV). These mechanical properties are undoubtedly related to the structural features reflected in the surface replicas.

E. Mechanical Properties of Carbon Fibers

The mechanical properties data for the samples used in this study are given in Table IV. The values for "Thornel" 40 fulfill or exceed our production standards (250 x 10³ lb/in.² for tensile strength and 40 x 10⁶ lb/in.² for the Young's modulus). The "Thornel" 25 sample fell somewhat below our specifications of 180 x 10³ lb/in.² for tensile strength and 25 x 10⁶ lb/in.² for the Young's modulus.

F. Results and Discussion of Chemically Treated "Thornel" 40

One sample of the very well characterized "Thornel" 40 (lot 03107-T-5) was treated chemically. The treatment with standard chromic acid cleaning solution at 50°C for 5 minutes was used because the previous studies in our laboratories showed a two-fold improvement in interlaminar shear strength in NOL rings with graphite yarn treated in this manner.⁶



6000x

6000x

6000x

10150x

10150x

N-18385

Figure 4. Electron Micrograph of Carbon Yarn VYB 70 1/2 (Lot No. 602 137-5)



14300x

14300x

10150x

14300x

14300x

N-18386

Figure 5. Electron Micrograph of Graphite Yarn WYB 85 1/2 (Lot No. 603097)



10150x

14300x

10150x

14300x

14300x

N-18387

Figure 6. Electron Micrograph of "Thornel" 25 Yarn WYD 115 1/2 (Lot No. 03107T-3)



14300x

10150x

10150x

10150x

14300x

N-18388

Figure 7. Electron Micrograph of "Thornel" 40 Yarn WYD 130 1/2 (Lot No. 03107T-5)



10150x

10150x

10150x

10150x

6000x

Figure 8. Electron Micrograph of High Modulus Graphite Yarn (Lot No. S-504307-1)
N-18389



10150x

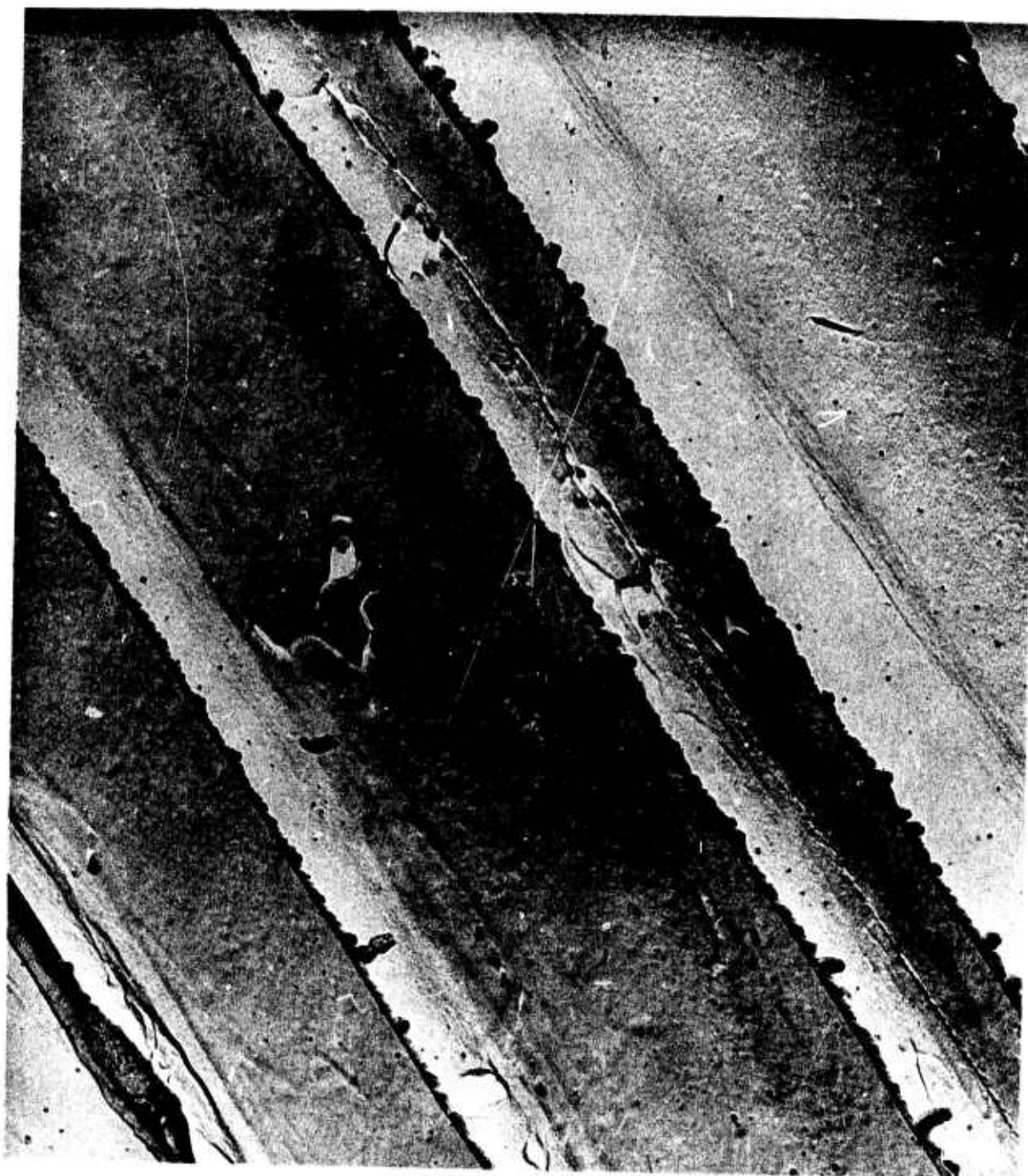
10150x

10150x

14300x

14300x

Figure 9. Electron Micrograph of "Thorne" 40 (Lot No. 03107T-5)
after Treatment with Chromic Cleaning Solution
N-18390



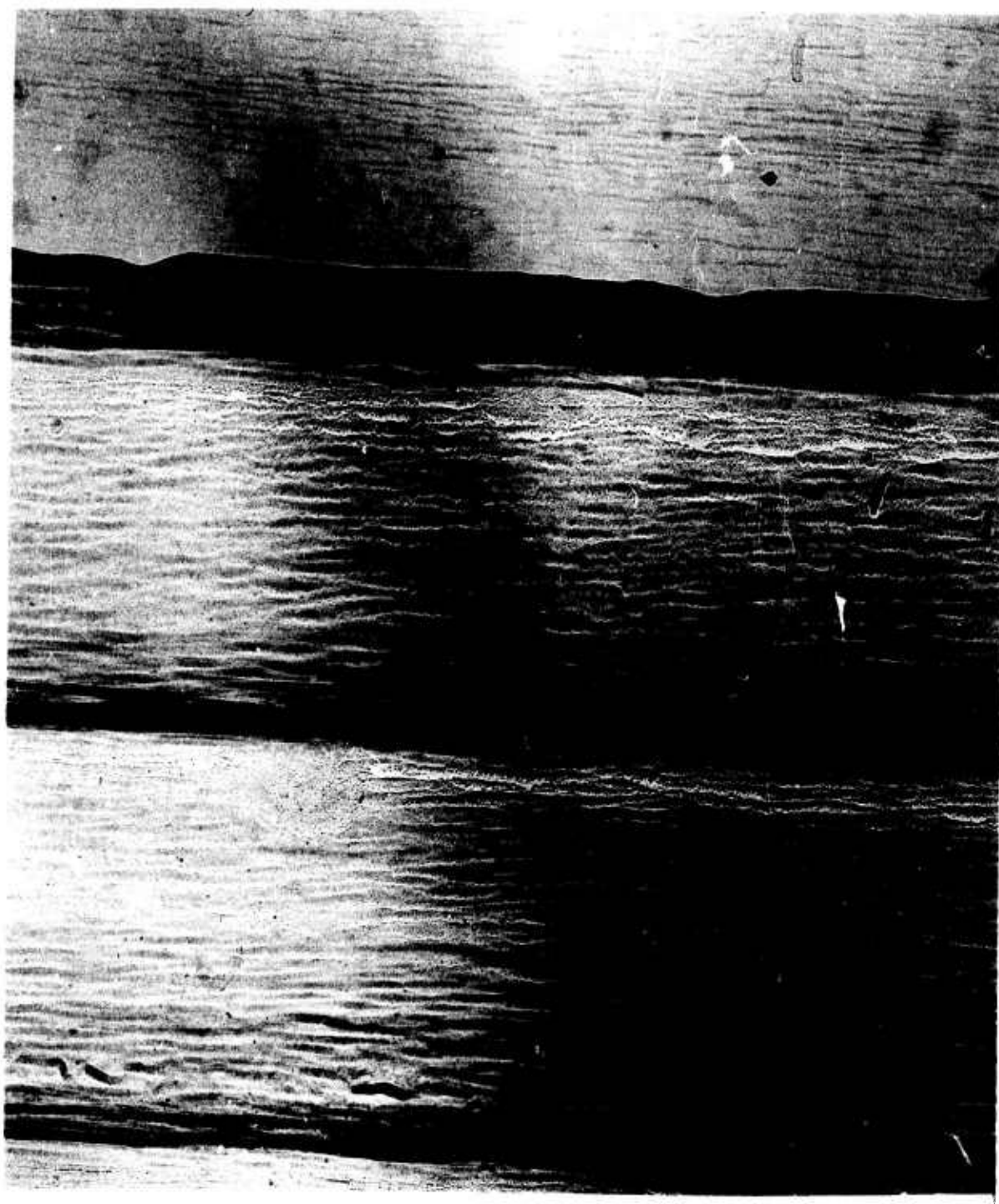
N-18391

Figure 10. Electron Micrograph of Carbon Yarn Mag. 40,600x



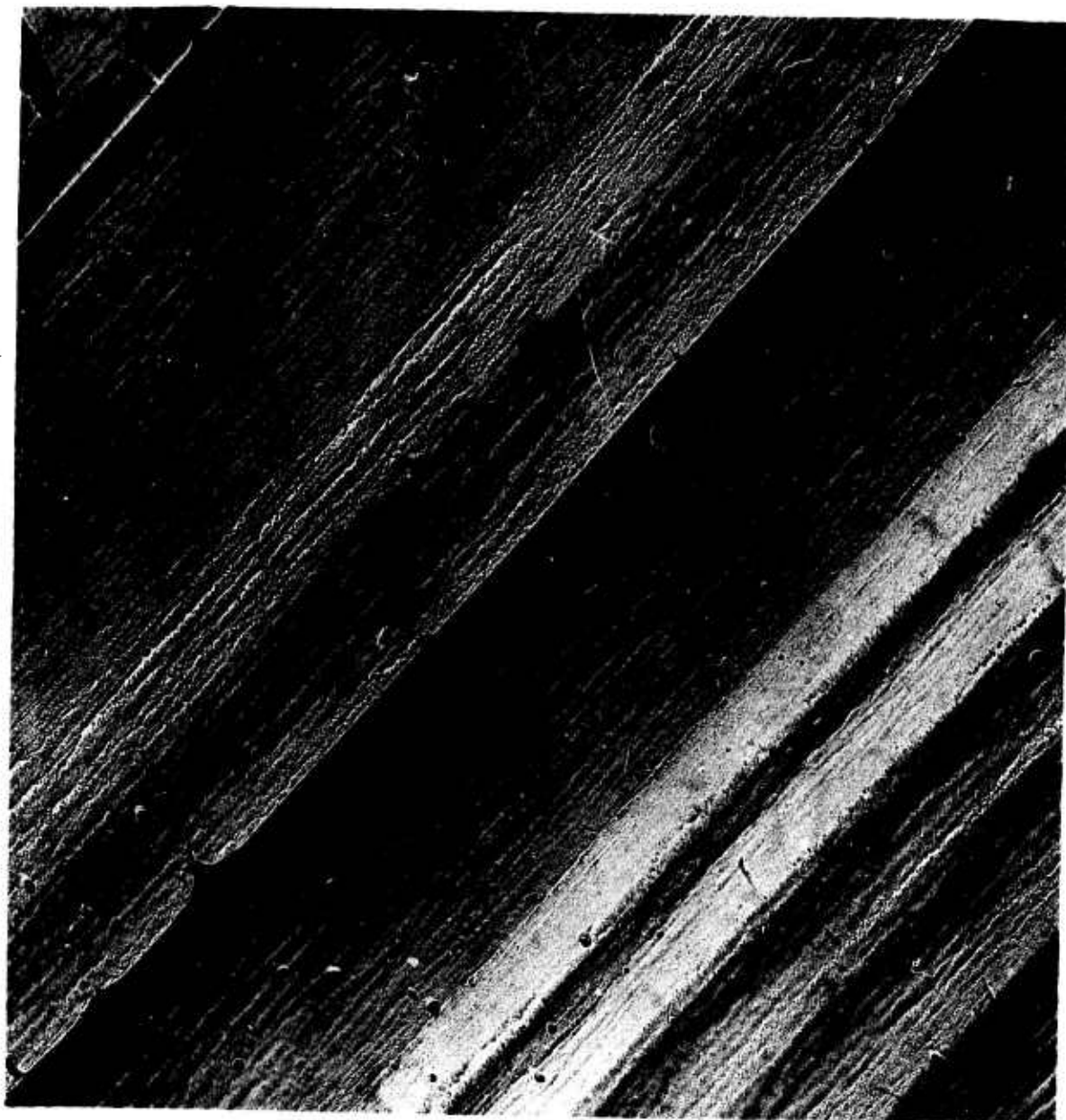
N-18392

Figure 11. Electron Micrograph of Graphite Yarn Mag. 57,200x



N-18393

Figure 12. Electron Micrograph of "Thornel" 25 Mag. 57,200x



N-18394

Figure 13. Electron Micrograph of 'Thornel' 40 Mag. 57,200x

TABLE IV
MECHANICAL PROPERTIES DATA ON CARBON FIBERS

Type of Fiber Lot Number	Cross Section		Tensile Strength		Young's Modulus	
	Average (μ^2)	Coefficient of Variation (%)	(10^3 lb/in. ²)	Coefficient of Variation (%)	(10^6 lb/in. ²)	Coefficient of Variation (%)
Carbon Yarn VYB70-1/2 Lot 602127-S	81.67	9.2	92	19.3	5.2	9.2
Graphite Yarn WYB85-1/2 Lot 603 097	72.44	8.45	76	19.1	5.3	11.9
"Thornel" 25 WYD115-1/2 Lot 03107T-3	48.75	10.5	129	29.2	22.2	15.6
"Thornel" 40 WYD130-1/2 Lot 03107T-4*	33.94	10.9	242	22.5	49.2	21.7
"Thornel" 40 WYD130-1/2 Lot 03107T-5*	35.16	13.5	254	22.8	44.6	7.31
Experimental Sample Lot S-504 307-1	34.12	6.3	181	30.7	38.7	32.0

* These samples have been run on two different days

The determination of surface area and porosity sample revealed the surprising fact that both the surface area and the pore volume are reduced by chromic acid treatment (see Table V). The most significant effect of this treatment seems to be a pronounced shift in the pore size distribution, best reflected in Figure 14 which shows a sharp increase in the fraction of the pores of large diameters. These pores will be undoubtedly much easier penetrated by the epoxy resin than the smaller ones, thus providing for an improved interlocking between the resin and the matrix. None of these differences are visible in the electron micrographs (Figure 15). Without discounting the possible significance of the chemical effects of oxidation treatments of the carbon fiber and their role in promoting adhesion, one may assume that these findings indicate that the pore-size distribution on the fiber surface should be included among the various parameters affecting the micromechanics of the carbon fiber composites. Unfortunately, the treatment with chromic acid cleaning solution appreciably deteriorates the mechanical properties of the fiber, particularly the tensile strengths as shown in Table VI.

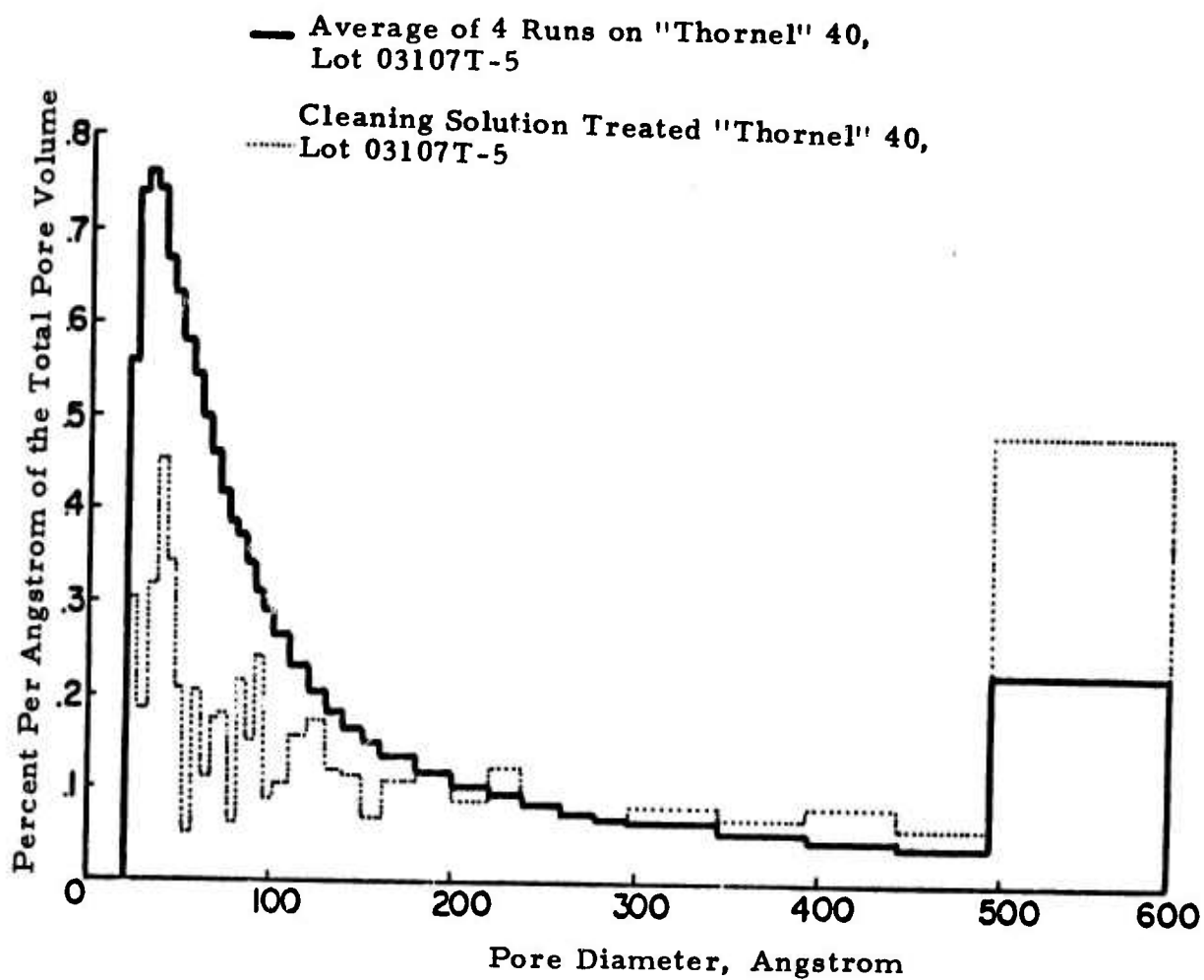
Herrick⁷ studied extensively the treatment of "Thornel" 25 with nitric acid and found that it, too, improved the interlaminar shear strength and did not deteriorate the mechanical properties of the fiber. In correlating the composite strength with the surface area and the chemical functionality of fibers, Herrick concluded that, despite the increased surface area, chemical functionality was a determining factor in improved adhesion.

TABLE V
CHANGE OF POROSITY AND SURFACE AREA
AFTER TREATMENT WITH CHROMIC ACID CLEANING SOLUTION

Sample	Surface Area (m ² /g)	Pore Volume (cc/g)	Pore Diameter, Angstrom		
			Upper*** Quartile	Median	Lower Quartile
"Thornel" 40 Lot 03107T-5	1.4	.00306	444	144	57
After Treatment with Cleaning Solution at 50° C for 5 min.	.3*	.00251	550	475	170

* Determined on one sample only, Past experience with similar samples indicates that the error in these determinations could be $\pm .4$ m²/g.

** For explanation see Table I



N-18288

Figure 14. A Comparison of Treated and Untreated "Thornel" 40



Figure 15. "ThorneI" 40 (Lot No. 03107T-5) after Treatment with Chromic Acid
N-18395

TABLE VI
MECHANICAL PROPERTIES OF CHEMICALLY TREATED "THORNEL" 40
(Lot 03107-T-5)

	Cross Section		Tensile Strength		Young's Modulus	
	Average	Coefficient of Variation	(10 ³ lb/in. ²)	Coefficient of Variation (%)	(10 ⁶ lb/in. ²)	Coefficient of Variation (%)
None	35.16	13.5	254	22.8	47.6	7.31
Chemical Acid "Cleaning Solution" at 50° C for 5 min.	35.75	5.98	152	12.2	41.5	10.3

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13. ABSTRACT

The bibliography presented in the first part of this report lists literature sources on the surface properties of carbon and graphite, in bulk and fiber form, selected from the point of view of their relevance to the technology of composite materials. The topics considered are: morphology, surface compounds, wetting and adsorption properties of different forms of carbon, and the results of studies specifically directed toward modifying the surface of carbon and graphite fibers in order to improve their performance in composites.

The second part contains the most recent experimental data on mercury density, pore-size distribution and surface area of low modulus carbon, and graphite fibers, and of high modulus "Thornel" 25 and "Thornel" 40 fibers. Some preliminary results of surface treatment of "Thornel" 40 with chromic acid solution are also given.

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